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Effects of organic acids of different molecular size on phosphate removal by HZO-201 nanocomposite

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HIGHLIGHTS

- Three diverse-sized organic acids have distinct effect on P-PO$_4^{3-}$ uptake by HZO-201.
- The small-sized GA reduce capacity of P-PO$_4^{3-}$ by competing for sites directly.
- The middle-large TA inhibit P-PO$_4^{3-}$ adsorption rate due to pore blockage.
- The largest HA pose little impact on P-PO$_4^{3-}$ removal because of size exclusion.
- The organic acids compete for R-N$^+$(CH$_3$)$_3$ of HZO-201 instead of the nano-HZO sites.

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ABSTRACT

Various organic acids in wastewater effluent could significantly influence the performance of phosphate adsorbent. This study focused on the effects of organic acids of different-molecular-size on phosphate adsorption by a novel nanocomposite HZO-201. Three organic acids (gallic acid (GA), tannic acid (TA) and humic acid (HA)) with distinct molecular size (HA > TA > GA) were chosen for this purpose. Both isotherm and kinetic tests of phosphate adsorption were conducted in the single-phosphate and binary system, and a series of microscopic techniques (i.e., XPS, FT-IR and SEM-EDX) and N$_2$ adsorption-desorption test were employed to explore the underlying mechanism. It was found that GA could greatly weaken phosphate adsorption capability of HZO-201 by directly competing for ammonium group on the nanocomposite, TA exhibited significant inhibition on phosphate adsorption rate mainly through pore constriction/blockage, while HA posed negligible impact on phosphate adsorption because of the size exclusion effect. It was also observed that although GA, TA and HA showed substantial influence on bulky HZO due to complexation, their impact on the nano-HZO loaded inside HZO-201 was little. The covalently bounded ammonium group and the networking pore structure of HZO-201 may play important roles in it.

1. Introduction

Excessive release of phosphorus into water body has frequently caused undesirable eutrophication on a global scale (Schelske, 2009). Currently, varieties of techniques have been proposed for enhanced removal of phosphate from municipal wastewaters (Mino et al., 1998; Sherwood and Qualls, 2001; Loganathan et al., 2014). Among them, adsorption has been extensively focused on due to its prominent efficiency of phosphorus separation as well as simple operation, low running costs, and potential of phosphorus recovery. But conventional sorbents exhibit inferior selectivity for adsorption toward phosphate over coexisting inorganic species including SO$_4^{2-}$, NO$_3^-$, Cl$^-$ and HCO$_3^-$ (Acelas et al., 2015). Thus, various new-type adsorbents have been developed for selective removal of phosphate from secondary effluent (Mullan et al., 2006; Wilsenach et al., 2007; Saha et al., 2009; Zhang et al., 2016a ,b). Among them, metal hydroxide-based nanocomposites were drawing ever-increasing attentions in wastewater treatment (Pan et al., 2009, 2014; Chen et al., 2015). Typically, this type of nano-composites could be synthesized by embedding metal oxide nanoparticles into the inner pores of anion exchange resins. The obtained materials possess two types of adsorption sites for phosphate removal, the ammonium groups covalently bounded onto the polymeric matrix of the host and the loaded metal oxides

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nanoparticles. The ammonium group could facilitate preconcentration and permeation of phosphate inside the nanocomposites, and the loaded metal hydroxide nanoparticles could specifically adsorb phosphate mainly through inner-sphere complexation (Chen et al., 2015). This series of nanocomposites showed superior selective adsorption toward phosphate than conventional sorbents in the presence of coexisting anions at high levels, and some of them have been successfully applied in pilot-scale treatment plants for phosphorus removal and water purification.

However, the fact cannot be ignored is that besides the above-mentioned inorganic anions, organic matters also coexist with phosphorus in natural water body and municipal sewage treatment effluent (Kim et al., 2015). It has been confirmed that the organic matters caused notable impact on the performance of phosphate adsorbents, such as capacity loss and fouling (Beril Gönder et al., 2006; Abrams, 1982). Specifically, the organic acids (i.e., humic acid, tannic acid, gallic acid) which account for 14–60% (in mass) of organic matters in WWTP bio-effluents (Kim and Dempsey, 2008, 2010, 2012), obviously disturb the separation of phosphate from water (Kim, 2015). Compared with other categories of organic matters in effluent, organic acids were preferentially sequestrated by adsorbents such as ion exchange resins (Chen et al., 2002) and MIEX© magnetic resins (Kim et al., 2015; Kim, 2015) during phosphate separation from secondary effluent. The strong-base anion exchanger exhibited 15–20% capacity losses in gallic acid (GA) or tannic acid (TA) containing solutions during the column cycling tests (Abrams, 1982). Another study revealed GA or TA molecules decreased the adsorption capacity of nitrate-nitrogen onto D201 resin (Song et al., 2013). The co-existed humic acid (HA) was found to expose a slight capacity drop of phosphate onto La-201 according to a latest study (Zhang et al., 2016a). These organic acids abundant in aromatic carboxyl or phenolic groups yielded remarkable impact on inorganic anions sequestration by resins, ascribed to their high affinity to the positively charged ammonium groups of resin (Abrams, 1982; Song et al., 2013).

Available studies revealed that molecular size of organics might be a significant factor referring to the influence on adsorptive removal of anion pollutants from water. Organic matters with certain molecular size could permeate into inside pore channels of adsorbents to block the inner pores (Zietzschmann et al., 2014). Li et al. (2003a) discovered that dissolved organic matters with smaller molecular size decreased adsorption capacity of particle active carbon towards atrazine through direct site competition, while those with larger molecular size affected the adsorptive kinetics through pore constriction/blockage. It was also considered that the decrease of micropore volume of active carbon was mainly due to adsorption of the smaller organic molecules, whereas the pore constriction/blockage was primarily resulted from larger molecules occupying mesopore area (Pelekani and Snoeyink, 2001). But contrarily, the inconsistent results also had been drawn that larger TA molecule exhibited more blockage in micropores of black carbon, while the smaller GA posed no apparent impacts on both micro- and mesopores (Qiu et al., 2009). In addition to the influence of adsorbents' pore structure, organic matters diffusing inside the sorbents could occupy the active sites. For instance, some weak organic acids such as GA and TA could compete for quaternary ammonium groups of strong-base anion resins by aromatic acidic groups of organic acids, and lead to a dramatical decrease of capacity towards NO_3^- anions (Song et al., 2013).

One side, although the effect of molecular size of organic acids on structural characteristic and adsorptive ability of sorbents have been examined aiming for removal of some anionic pollutants, the influence on phosphate sequestration from water is still not clarified. On the other hand, available studies only focused on the traditional sorbents with single active site, such as ion exchange resin and active carbon. Similar investigation on metal hydroxide-resin hybrid adsorbents with unique composite structure is scarce. During our pilot trial of water purification with metal hydroxide-resin hybrid adsorbents, the reduction of organic matters was concurrently observed when phosphate removed (Yang et al., 2015). Therefore, to further improve the efficiency of phosphate sequestration by the hybrid materials, it is necessary to reveal the impact and intrinsic mechanism of organic acids with different molecular size on adsorption of phosphate.

In this research, a lately developed nanocomposite HZO-201 was employed as sorbents for phosphate adsorption. HZO-201 features cross-linked polystyrene supporting matrix covalently bonding ammonium groups and impregnated HZO nanoparticles. HZO-201 has been proved effective for phosphate removal when high-level inorganic anions coexisted (Chen et al., 2015). Three kinds of organic acids, HA, TA and GA, were chosen to evaluate their affection on adsorption of phosphate onto HZO-201 in view of their wide distribution in secondary effluents and marked difference in molecular size. Batch experiments in separated or binary system were conducted to test the effects of the three organic acids on phosphate adsorption by HZO-201. Spectroscopy method was employed for mechanism analysis.

2. Materials and method

2.1. Materials

All chemicals involved in this study were of analytical grade. $ZrOCl_2 \cdot 8H_2O$, GA, TA and HA (sodium salts) were all purchased from Sigma-Aldrich (USA). The structural formulas of the organic acids were described in Fig. S1. The polymer host D201, a macroporous strongly basic anion exchanger, was supplied by Zhengguang Industrial Co., Ltd. (Hangzhou, China). The diameter of D201 beads were in the range of 0.6–0.8 mm. Prior to use, D-201 was subjected to extraction with ethanol in a Soxhlet apparatus to remove possible residual impurities. The aqueous stock containing 1000 mg P/L was prepared by dissolving predetermined KH_2PO_4 into deionized water (18.25 MΩ cm). Desired amount of GA (TA or HA) were also separately dissolved with deionized water to obtain the stock solution of 1000 mg TOC/L.

2.2. Preparation and characterization of nanocomposite adsorbents

The hybrid adsorbent HZO-201 was synthesized by means reported in our previous study (Pan et al., 2013). In brief, 25 g of polymeric host D201 was added into mixed solution of ethanol, HCl and $ZrOCl_2 \cdot 8H_2O$, subsequently stirred for 12 h continuously. The Zr(IV) saturated D201 were filtered out and transferred into 200 mL of 10 wt % NaOH solution with continuous stirring for another 12 h. The resultant beads were then immersed in 1.0 M NaCl solution to convert the residual OH^- into Cl^-. Finally, the HZO-201 composites were obtained after air-drying at 333 K for 12 h.

HZO-201 beads preloaded with organic acids were sampled at the initial GA (TA or HA) concentration of 20 mg TOC/L. The beads were rinsed with distilled water for several times and subsequently vacuum-dried for a week at 323 K. Losses of organic acids after rinse were negligible. Both fresh and loaded HZO-201 were examined for their specific surface area and pore size distribution by N_2 adsorption-desorption tests at 77 K (Micromeritics ASAP-2010C Instrument, Norcross, GA). Standard